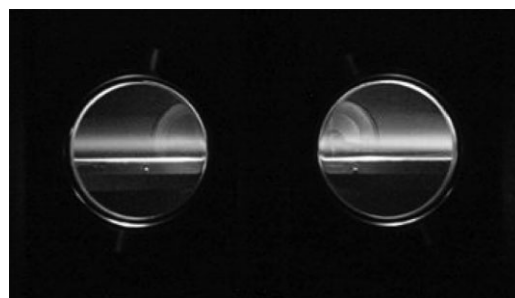


Physio-Chemical Modifications of Polystyrene and Poly(propylene) Surfaces by Electron Beam-Generated Plasmas Produced in Argon

Evgeniya H. Lock,^{*,a} Scott G. Walton, Richard F. Fernsler

Pulsed, electron beam generated plasmas produced in argon were used to modify the surfaces of polystyrene and poly(propylene). The influence of plasma parameters including duty factor, plasma period and exposure time on the surface chemistry, energy and morphology was investigated. In these plasmas, the energy of ions striking the surfaces was modest (≤ 5 eV) and comparable to the bond strength of most polymers. Despite the lack of reactive species in the background, a substantial modification in the chemical composition of the polymer surface occurred, leading to a significant increase in surface energy. These changes occurred without a significant increase in surface roughness, or loss of material due to etching. Indeed, the surface morphology of polystyrene was practically unchanged, whereas the surface of poly(propylene) became smoother with plasma exposure. Based on theoretical estimations, the ions play major role in the modification of polymers.



Introduction

In recent years, there has been remarkable growth in the use of polymers, due to their relatively low cost and desirable chemical and physical characteristics (high strength-to-weight ratio, resistance to corrosion, etc.). However, fundamental differences between polymers and other engineering materials have created numerous technical challenges that must be overcome. An important example is the characteristically low surface energy of polymers, which typically results in poor adhesion. But

since adhesion is a surface property, it is possible to modify this layer without affecting the desirable bulk properties.

Different plasma technologies have been successfully applied to treat polymers for a long time, which has resulted in a number of publications.^[1–5] In general, plasmas create a mix of inert and reactive neutral and charged species, as well as UV and vacuum UV photons that affect the physio-chemical characteristics of the polymer surfaces. All of these species take part in surface modifications, but the relative importance of each depends on the type of plasma and the operating conditions. For example, most of the plasma technology up to date relies on the discharge generation using different sources including DC, RF, microwave, etc. . . In all of these cases, an electric field is supplied and electrons are heated to an energy sufficient to sustain the plasma. However, the average electron energy is much lower than is required for ionization. In fact, the electron energy distribution falls off rapidly at high energy, so more energy is spent on gas

E. H. Lock, S. G. Walton, R. F. Fernsler

Plasma Physics Division, Naval Research Laboratory, 4555 Overlook Ave., Washington DC 20375

Fax: 1-202-767-3553;

E-mail: evgeniya.lock@nrl.navy.mil

^aNRL/NRC Postdoctoral Research Associate

excitation and dissociation compared to ionization. Thus, more metastables, radicals, and photons are produced compared to ions. All of these species possess either potential or kinetic energy that can be delivered to the surface: metastable energies are in the range 10–20 eV,^[6] photon energies from UV are 3–40 eV,^[6] electron kinetic energies are from 0 to 10 eV^[6] and ion kinetic energies are higher than 10 eV.

In this work, we apply an electron beam-generated plasma source developed at the Naval Research Laboratory. It uses a high-energy electron beam (2 keV), which, when injected into the gas, causes its ionization and produces a high-density plasma. The electrons and ions produced during ionization form the plasma. Unlike discharges, no external fields are used to heat the electrons, so they are rapidly cooled. As a result, the electron temperature is lower than in discharges,^[7] which leads to lower plasma potential; therefore the ion kinetic energies at adjacent surfaces are also small (< 5 eV).^[8,9] Moreover, a lower production of excited species can be expected in these plasmas as well. The main objective of this study is to investigate the effect of a high flux ions with low kinetic energies on polymer surface chemistry and morphology. Well studied polymers, including polystyrene and poly(propylene), were chosen to help understand the differences between electron beam produced plasmas and conventional discharge treatments. Limiting the working gas to argon eliminates the possibility of chemically driven surface reactions associated with reactive species generated in the gas phase and allows for establishing a baseline for further investigations. An attempt was also made to determine if chain scission or cross-linking was the dominant mechanism responsible for the surface modification.

Experimental Part

Materials

The polymers used in this work have been studied previously by researchers using RF plasma sources^[6,10] and thus the results can be directly compared. Polystyrene (Sigma Aldrich, $\bar{M}_w \approx 280\,000$ by GPC) and isotactic poly(propylene) (Sigma Aldrich, $\bar{M}_w \approx 340\,000$, $\bar{M}_n \approx 97\,000$ and melt index 4 g/10 min) supplied in pellet form were dissolved and spin-coated on top of 300 μm thick, prime grade silicon wafers (Silicon Quest, Inc.).^[11] Because of the amorphous structure of polystyrene, dissolving it is relatively easy. Toluene anhydrous 99.8% (Sigma Aldrich) was chosen as a solvent for polystyrene. Heating of the polystyrene solution in toluene (2 wt.-%) to 50 °C for 2 h was sufficient to completely dissolve the solid polymer. No specific measures were undertaken in the spin-coating process. In the case of poly(propylene), decaline anhydrous 99% purity (Sigma Aldrich, mixture of cis and trans) was used as a solvent. Poly(propylene) was dissolved for three hours in hot decaline solution (2 wt.-%) with the temperature

above 160 °C. The solution was transported with droppers that were preheated to 120 °C. The Si wafer itself was heated to temperatures above 160 °C to ensure uniform surface wetting. The spin coater chuck was heated to about 60 °C as well.

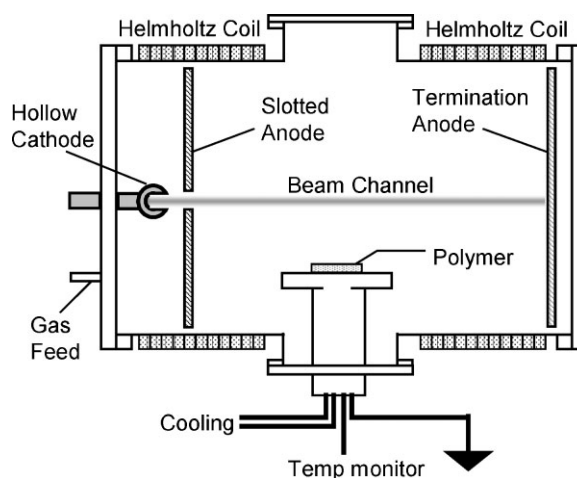
For both polymers, the films were spin-coated at 3 000 rpm for 1 min. The film thickness of the polymer films was approximately 100 nm, varying slightly (< 5 nm) from sample to sample. The films were positioned in a dessicator for 24 h to ensure complete solvent evaporation.

Electron-Beam Plasma Source and System

The experimental apparatus has been discussed previously,^[9] and is shown in the schematic of Figure 1. The system vacuum was maintained by a 250 l·s⁻¹ turbo pump, with a base pressure on the order of 10⁻⁷ Torr. The operating pressure was achieved by introducing argon (purity > 99.9999%) through the mass flow controllers and throttling the turbo pump using a manual gate valve. The electron beam was produced by applying a 2 kV pulse to a linear hollow cathode for a selected pulse width and duty factor. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further downstream. The electrode beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1 cm × 25 cm) and the anode-to-anode length (40 cm). Beam spreading from collisions with the background gas was suppressed by a co-axial magnetic field produced by a set of external magnetic field coils. The samples were placed on a 10.2 cm diameter stage located at 2.5 cm from the edge of the electron beam. Because the beam is collimated, no high energy electrons will hit the surface of the material. The stage was held at ground and room temperature.

Plasma Treatment Parameters

All of the experiments were conducted at constant pressure of 50 mTorr. The hollow cathode voltage and current were typically



■ Figure 1. Schematic of the electron beam plasma source.

2 kV and 14 mA, respectively. The variation in current was less than 10% for all experiments. Magnetic field strength was 150 G. Most of the experiments were conducted with a flow rate of 50 sccm with the exception of an experiment using a flow rate of 75 sccm to study the influence of the residence time. The influence of plasma parameters, including plasma period, duty factor and plasma treatment time on polymer surface modification was studied. The terms plasma period and duty factor used in the paper are defined as follows: plasma period is the time between two consecutive pulses. This period comprises the beam pulse width (when plasma is produced), the afterglow when the plasma decays, and then a time when no plasma is present. The duty factor is the ratio of the plasma on-time to the plasma period. The plasma treatment time is the total plasma exposure time and is defined as the total experimental time multiplied by the duty factor. Note that, for simplicity, the plasma decay in the afterglow time is not considered when reporting plasma treatment time. A summary of the experimental conditions is shown in Table 1.

Residual Gas Analysis

A residual gas analyzer (Stanford Research Scientific) was used to determine the background gas composition at 10^{-7} Torr (base pressure) and 10^{-4} Torr. The RGA characteristics include scans from 1 to 50 amu, electron energy of 70 eV, CEM voltage of 1 000 V and a filament current of 1 mA. An average of 50 scans was taken for each measurement.

Water Contact Angle Measurements

Contact angle measurements were performed with a goniometer (Rame'-Hart, Inc.). Drops of selected test liquid, in this case water, were positioned on the surface with a micro-syringe. The droplet volume was 2 μ l. The contact angles of both sides of three drops were measured and averaged for each sample.

Atomic Force Microscopy

The polymer surface morphology was studied at various scales using an atomic force microscope (Nanoscope III, Veeco Metrology,

Santa Barbara, CA) operated in tapping mode. Surface images were obtained from $1 \times 1 \mu\text{m}^2$ and $20 \times 20 \mu\text{m}^2$ area scans using resolution of 256×256 pixels. The scan rate was adjusted depending on the size. The small areas of $1 \times 1 \mu\text{m}^2$ were scanned at a rate of 2 Hz, and the areas of $20 \times 20 \mu\text{m}^2$ were scanned at a rate of 1 or 1.5 Hz. The height scale was adjusted to accommodate the surface features. For a quantitative evaluation of the topography changes, root-mean square roughness was calculated from the surface height data z_i using:

$$R_q = \left[\frac{1}{N} \sum_{i=1}^N |z_i - \bar{z}|^2 \right]^{1/2} \quad (1)$$

where $\bar{z}$ is the mean height distance.

Ellipsometry

A V-VASE variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc) was used to estimate the polymer film thickness change with plasma treatment. Three different angles of incidence (55° , 60° and 65°) and wavelengths ranging from 190 to 2 250 nm were used to measure the real and imaginary parts of the complex reflectance ratio. The film thickness was determined using the following procedure. First, the thickness of the native SiO_2 layer on clean Si wafer was measured. Then, a multilayer Cauchy model was built, in which the SiO_2 layer thickness was fixed and the thickness of the polymer layer was evaluated.

Glass Transition Temperature Measurements

The glass transition temperature (T_g) measurements were performed by J. A. Woollam Co., Inc. using a M-2000 spectroscopic ellipsometer over the wavelength range from 206 to 1 700 nm. The angle of incidence was 70° . A temperature – dependent thickness was used to calculate the glass transition temperature for the polystyrene and poly(propylene) films. The polystyrene films were first heated to 140°C and held for 30 min to relax the film and remove the residual solvent. The film was then cooled at a

Table 1. Summary of experimental conditions.

Variable	Duty factor	Plasma period	Pulse width	Afterglow time	Treatment time
	%	ms	ms	ms	ms
1. Duty factor	10	10	1	9	2
	20	10	2	8	2
	40	10	4	6	2
2. Plasma period	10	10	1	9	2
	10	20	2	18	2
	10	40	4	36	2
3. Plasma exposure	10	20	2	18	2
	10	20	2	18	5
	10	20	2	18	10
	10	20	2	18	20

constant rate of $1\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ to $50\text{ }^{\circ}\text{C}$. The poly(propylene) film was first heated to $60\text{ }^{\circ}\text{C}$ and held for 10 min, then held at $40\text{ }^{\circ}\text{C}$ for 4 min to relax and stabilize the film. Then the film was cooled at a constant rate of $1\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ to $-16\text{ }^{\circ}\text{C}$. The rate of thickness change with temperature differs below and above T_g . Linear fits for the two portions of the thickness change were obtained, and the intersection point of the two curves determines the glass transition temperature. Due to the low temperatures, the temperature cell was purged with nitrogen during poly(propylene) film measurement. Otherwise, the sample surface would readily frost over at temperatures below $0\text{ }^{\circ}\text{C}$. Similar to the ellipsometry analysis above, the data was fit using Cauchy model and for poly(propylene) the fit was improved by including a small amount of absorption described using an Urbach exponential absorption tail. For both polymers, further fit improvement was achieved by introducing a surface layer of lower index, modeled as surface roughness.

XPS Measurements

Surface chemical analyses were performed using a commercial XPS system (Thermo VG Scientific Escalab 220i-XL), equipped with a monochromatic AlK α (1486.6 eV) source, a hemispherical electron energy analyzer (58° angle between monochromator and analyzer), and a magnetic electron lens. The nominal XPS spot size and analyzer field of view were less than 1 mm^2 . The X-ray source was operated at a power of 150 W. An electron takeoff angle of 45° , measured from the sample surface, was used in all XPS measurements. The survey scans were taken using a pass energy of 100 eV, dwell time of 100 ms, large area XL lens mode, and an energy step-size (resolution) of 1 eV. Si 2p, C1s and O1s spectra were taken with a pass energy of 20 eV, using 6 to 20 scans, a dwell time of 100 ms, large area XL lens mode, and an energy step size (resolution) of 0.1 eV. Pressure in the main chamber during these analyses was 2×10^{-9} Torr. The peaks were fit using Unifit with a convolution of Lorentzian and Gaussian line shapes. A linear combination of Shirley and linear functions was used to model the background, with the corresponding coefficients fit simultaneously with the peaks.

Results and Discussion

Background Gas Composition

For these studies, it was critical to ensure a pure argon environment. To verify this, residual gas analyzer measurements were conducted. Since the gas flow rates and the gate valve that regulates the pumping speed can be adjusted independently, these parameters were varied to determine the relative gas densities (Figure 2). At base pressure, (maximum pumping speed), water was the dominant species, followed by nitrogen and oxygen. When the pumping speed was reduced (the gate valve was adjusted to correspond to the same position used in experiments with 75 sccm argon and 50 mTorr of pressure), the amounts of oxygen, nitrogen, water, argon

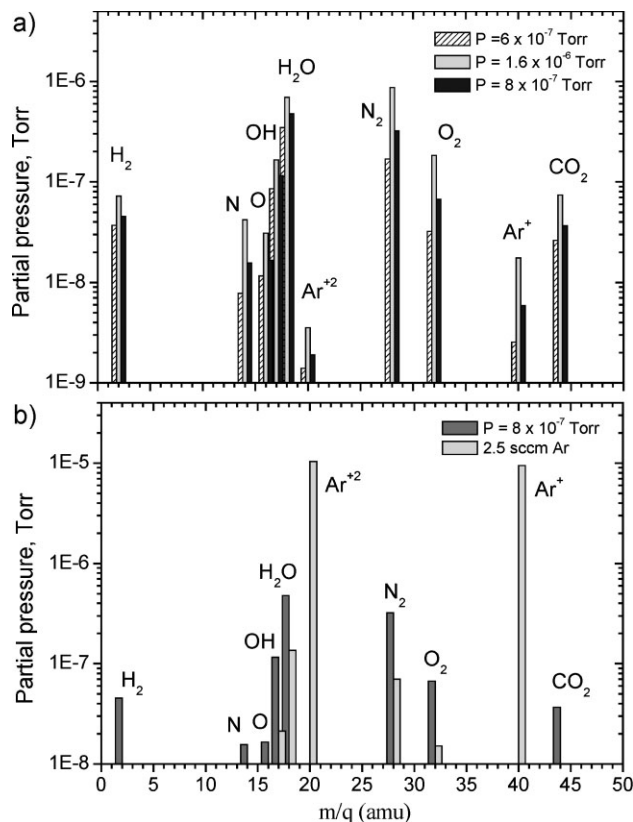


Figure 2. Background gas analysis: a) comparison between gas composition at full pumping speed and reduced pumping speeds corresponding to high flow ($p = 8 \times 10^{-7}$ Torr) and low flow ($p = 1.6 \times 10^{-6}$ Torr) processing conditions; b) comparison between gas composition at reduced pumping speed ($p = 8 \times 10^{-7}$ Torr) and with the addition of 2.5 sccm of argon ($p = 4 \times 10^{-6}$ Torr).

and CO_2 increased. However, when 2.5 sccm of Ar were added to the system at this pumping speed (Figure 2b), the amounts of oxygen and nitrogen did not change and remained well below the argon level.

When the pumping speed was further reduced to typical processing speeds (the gate valve was adjusted to correspond to the same position used in the experiments with 50 sccm argon and 50 mTorr of pressure), the levels of oxygen, nitrogen, water, argon and CO_2 increased only slightly (Figure 2a). These measurements show no contamination of the argon line, and that when much higher argon flow is present in the system, the amount of nitrogen and oxygen should be negligible and thus should not contribute to changes in the surface chemistry.

Surface Energy Characterization of Plasma Treated Polymer Surfaces

While the X-ray photoelectron spectrometry provides information about the average chemical composition in

the top 5 to 10 nm,^[12] the contact angle change is a function of chemical and morphological changes of the polymer surface. The surface energy characterization is thus a very important indication of the efficacy of the plasma treatment and the stability of the treated surface (surface aging). Aging time of the samples is defined as exposure of the polymers to air after plasma treatment. The contact angle of untreated polystyrene was 90°, which is a clear indication of a hydrophobic surface. As shown in Figure 3a, after plasma treatment the contact angle for polystyrene was reduced from 90 to 25° (for 2 min of treatment), which was measured 15 min after exposure to air. The treatment time, plasma period and duty factor variation did not have a strong influence on the contact angle obtained immediately after treatment ($\pm 3^\circ$). After 1 h the contact angle reached 35°, and then a very slow change to the equilibrium angle of approximately 45° after 24 h was observed. This angle did not change further with time – over a 24 d period. The contact angle of untreated poly(propylene) was 100°. A contact angle of 45° was measured 15 min after air exposure of plasma treated poly(propylene), as shown in Figure 3b. Unlike polystyrene, this angle did not change significantly thereafter. A similar phenomenon of production of stable polymer surface after plasma exposure was reported by France et al.^[10] for polystyrene when the O/C ratio was 0.2. As with polystyrene, the treatment time, duty factor and

plasma period variation had only a small effect on the final poly(propylene) surface energy.

The hydrophobic recovery of the polymer surface after plasma exposure has been reported before,^[6,13–15] and is due to the fact that the polar groups grafted on the surface move toward the bulk of the material until equilibrium is reached. At the same time, other hydrophobic low molecular weight fragments migrate to the surface from the polymer bulk. For both polymers, the contact angle was reduced by a factor of two even after aging, suggesting that the surface energy was significantly increased.

Morphology Study of Plasma Treated Polymer Surfaces

When performing atomic force microscopy, the scan size should be chosen to reflect the surface features since the value of surface roughness depends on the scanned area size. It was found that for polystyrene^[11] the RMS roughness did not change when the scanned area was increased from $1 \times 1 \mu\text{m}^2$ to $10 \times 10 \mu\text{m}^2$, so the scan area chosen was $1 \times 1 \mu\text{m}^2$. For poly(propylene)^[11] the RMS roughness of the untreated samples increased from 2 nm for $1 \times 1 \mu\text{m}^2$ scanned area to 8 nm for scan areas of $20 \times 20 \mu\text{m}^2$ and did not change when scan size was increased to $50 \times 50 \mu\text{m}^2$. Therefore, the RMS roughness for poly(propylene) reported in this study is for scan areas of $20 \times 20 \mu\text{m}^2$.

The atomic force microscope images, in Figure 4, show a comparison between untreated and treated (5 min treatment) polystyrene and poly(propylene). It is obvious from the images that the surface features for both polymers did not change significantly. This suggests that the sputtering of the surface was minimal, as was confirmed using etch rate analysis (discussed below). Furthermore, in the case of polystyrene (Figure 5), the surface roughness first decreased from 0.6 nm for untreated polymer to 0.4 nm after 10 min, and then increased to 0.5 nm after 20 min of plasma treatment. The surface roughness decreased with duty factor (Figure 5), and the reduction was independent of the plasma period for constant treatment time (results not shown). Since the atomic force microscope has atomic resolution, it can be concluded that the plasma had little or no effect on surface roughness. For poly(propylene), the initial surface roughness was approximately 9 nm, varying slightly from sample to sample. Given this variation, the relative changes in surface roughness are shown in Figures 6. The surface roughness decreased to different levels when the treatment time and duty factor were varied. It decreased by 7% after 2 min of plasma treatment and for periods of 10 ms or more. When the plasma treatment time was increased from 2 to 20 min (Figure 6), a 14% decrease in surface roughness was observed. Changes in

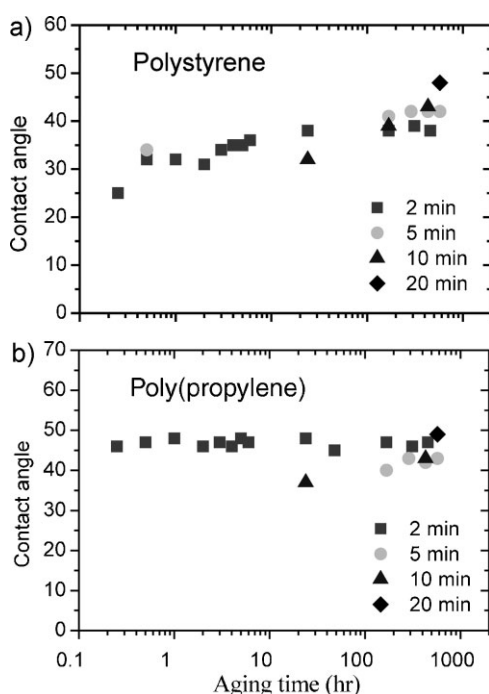


Figure 3. Water contact angle measurement for a) polystyrene and b) poly(propylene) for variable treatment times (duty factor 10%, period 20 ms). The contact angles for untreated polystyrene and poly(propylene) were 90° and 100° respectively.

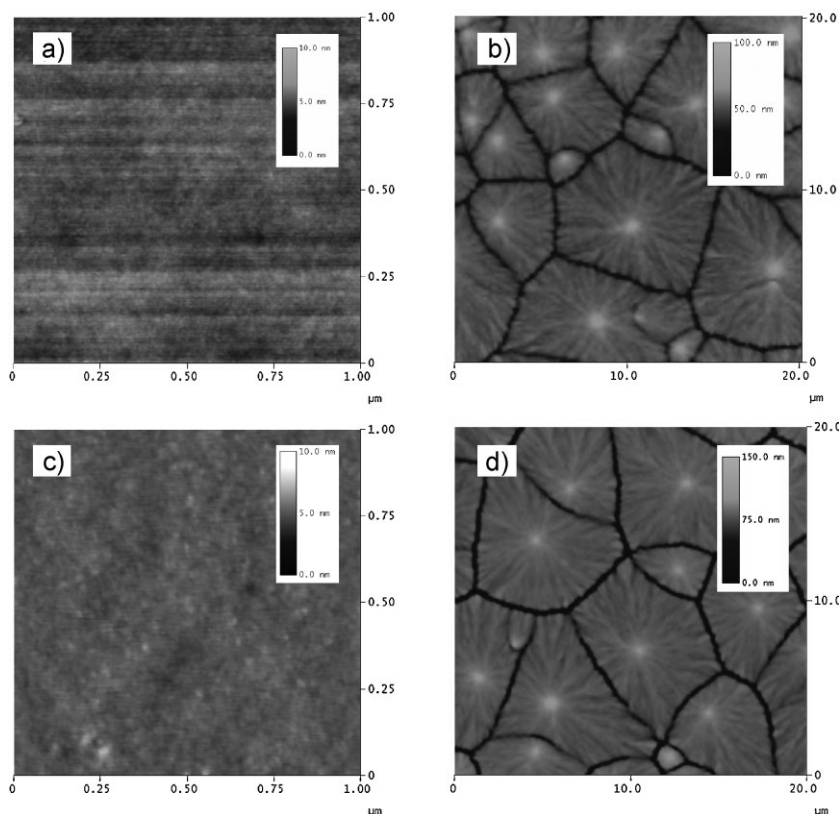


Figure 4. AFM images of polystyrene and poly(propylene): a) untreated and c) treated polystyrene; b) untreated and d) treated poly(propylene). Plasma treatment conditions include 10% duty factor, 20 ms period and plasma exposure time of 5 min.

polymer morphology was significantly changed by RF plasma treatment.^[16,17] Even when samples were placed downstream from the inductively coupled plasma source, surface roughness increased.^[18]

Etch Rates

The etch rates, defined as film thickness changes before and after treatment divided by the plasma treatment time, are shown in Figure 7. In order to understand when the most pronounced etching occurs, three different sets of experiments were conducted. In the first set, the duty factor and the treatment time were kept the same and the plasma period was adjusted to allow for the increase in the “plasma off” time. However, the etch rate was approximately the same for all studied cases, so etching is a function of direct plasma exposure. In the second set, the duty factor (i.e. the plasma on time) was increased for the fixed treatment time. This resulted in almost linear increase of the etch rate (Figure 7a), suggesting that the species generated during the pulse are responsible for the observed etching. In the third set of

experiments the effect of treatment time was investigated. It was found that the etch rates depended on the treatment time but not monotonically (Figure 7b). The rates increased for treatments up to about 5 min and then decreased for higher exposure times. This might be due to the removal of

duty factor had the largest influence on surface roughness. For a 40% duty factor, the decrease of surface roughness was as high as 30%. These results suggest that treatment by electron beam produced plasma in argon does not damage the surface for either polymer. In comparison,

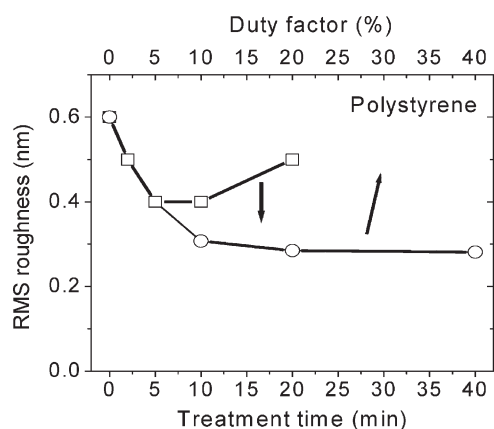


Figure 5. AFM analysis of polystyrene thin film as a function of treatment time (square symbols) and duty factor (circle symbols). Plasma treatment conditions include duty factor of 10% and period of 20 ms (square symbols); exposure time of 2 min and period of 10 ms (circle symbols).

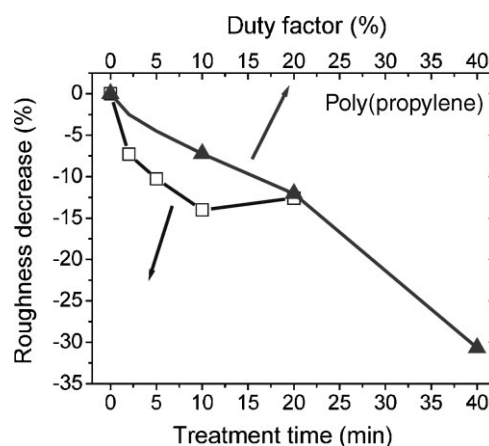


Figure 6. Roughness measurements of treated poly(propylene) films as a function of treatment time (open symbols) and duty factor (solid symbols). Plasma treatment conditions include duty factor of 10% and period of 20 ms (open symbols); exposure time of 2 min and period of 10 ms (solid symbols).

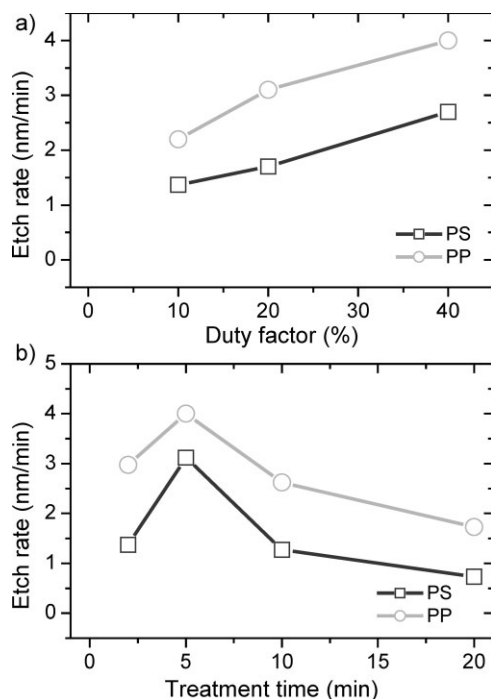


Figure 7. Etch rates for polystyrene and poly(propylene) as a function of (a) duty factor and (b) treatment time. Plasma treatment conditions include a) exposure time of 2 min and period of 10 ms; b) duty factor of 10% and period of 20 ms.

low molecular weight contamination fragments from the polymer surface early in time. It should be pointed out that in all cases the etch rates are very low (maximum $4 \text{ nm} \cdot \text{min}^{-1}$). The etch rates for polystyrene were lower than for poly(propylene), and this is due to its lower Ohnishi parameter ($O_{\text{PS}} = 2$, $O_{\text{PP}} = 3$),^[19] and the presence of the aromatic ring in the polystyrene structure which makes it more resistant to etching.^[20]

Glass Transition Temperature Measurements

The change in glass transition temperature can be a useful indicator of the interaction of argon ions with the polymer surface and can be influenced by material removal and surface reorganization. The samples used for the glass transition measurements were exposed to plasma for 2 min at a 10% duty factor. The removed material for polystyrene was 3 nm and 6 nm for poly(propylene). Thus, the change in glass transition temperature is mainly due to the surface chemical modifications, because the film thickness change is insignificant.^[21] Ellipsometry is an attractive technique for glass transition temperature estimations because it is not intrusive and does not require sample dissolution or particle incorporation. Furthermore, a film thickness of 100 nm provides a good range. The spectroscopic data fits were very good. For example, the film thickness of the polystyrene reference

sample was 105.254 nm with $\pm 0.0147 \text{ nm}$ variation and mean square error of 3.104. Using the spectroscopic data in conjunction with the Cauchy dispersion model also helps, because a wide range of spectral data (hundreds of Ψ - Δ data pairs) is modeled with only few parameters. The measurement/analysis methods were also consistent between the sample types for polystyrene, as well as for both poly(propylene) films (treated and untreated). Throughout the dynamic measurements, the mean square error was consistently low (less than 3). The index of refraction is included in the graphs as well, to show data consistency and was calculated based on the Cauchy dispersion model for transparent materials. After plasma treatment, the glass transition temperature of both polymers was changed: for polystyrene an increase by 2.5°C was observed, whereas a decrease by 0.4°C was detected for poly(propylene). The small variation in the glass transition temperature is due to the gentle plasma treatment of the polymer, i.e. the low ion energies. In comparison, when polystyrene ($\bar{M}_w = 212\,000 \text{ g} \cdot \text{mol}^{-1}$) was irradiated with 1 keV Ar^+ ions, an increase of 20°C of the glass transition temperature was measured.^[22] Even though the argon ions in the electron beam plasma have less kinetic energy compared to other plasma treatments, they caused sufficient chemical modification of the polymer surfaces (as will be shown later), and thus produced changes in the glass transition temperature. The small decrease in T_g for poly(propylene) is an indication of bond scission, i.e. methyl group cleavage formation. This results in low molecular weight fragments that form on the polymer surface (Figure 8b and d). On the other hand, free radicals may react with other chains to produce high-molecular weight fragments or crosslinks; these reduce the polymer free volume and make the molecular motion more difficult, thereby raising the glass transition temperature.^[23] This is the case for polystyrene (Figure 8a and c). Chain end groups have a significant effect on T_g as well.^[24] For example, polar groups increase the glass transition temperature by impeding bond rotation.^[23]

Chemical Modification of Polymer Surfaces

The survey spectrum of untreated polystyrene (Figure 9a) shows 100 at.-% carbon, with no Si impurities or oxygen in the chemical composition. From the survey spectrum of untreated poly(propylene) (Figure 10a), C1s is the dominant peak, and only small amounts of oxygen (0.3 at.-%) and Si (0.5 at.-%) were detected. The small amount of oxygen in the untreated poly(propylene) sample might be due to surface oxidation, while silicon might have arrived on the surface during wafer cleaving. After five minutes of plasma treatment and subsequent exposure to air, large amounts of oxygen functionalities were incorporated into

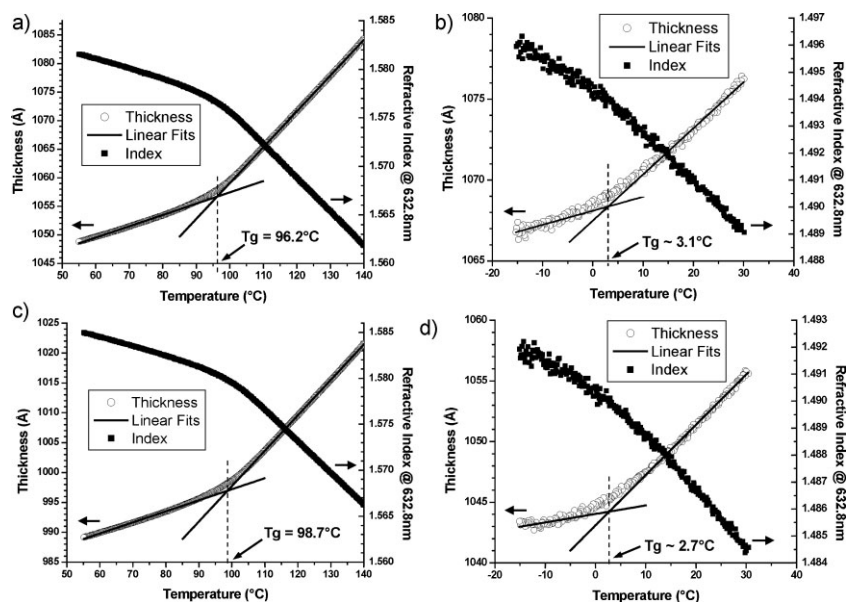


Figure 8. Glass transition temperature of a) untreated polystyrene, b) untreated poly(propylene), c) treated polystyrene and d) treated poly(propylene). Plasma treatment conditions were 10% duty factor, 2 min exposure time and period of 10 ms.

during or after plasma exposure. It can be concluded that the oxygen functionalities, observed after plasma treatment, were not due to vessel contaminations, were not carried with the argon flow, and did not come from the sample bulk. Instead, it is assumed that argon ions created chemically active sites on the polymer surface, mostly from hydrogen abstraction. Exposing the substrate to air after plasma treatment produced chemical changes as oxygen was introduced. A comparison of the high resolution C1s region of the XPS spectra for untreated and treated polystyrene and poly(propylene), shown in Figure 11, suggests that the plasma strongly changed both polymer surfaces. The experimental condition for this treatment was 10% duty factor and 20 min of treatment time. The untreated polystyrene has the $\pi-\pi^*$ shake-up structure, which is not present after treatment. The $\pi-\pi^*$ shake-up is characteristic of the aromatic ring and is

the polymers (Figure 9b and 10b): 11.58 at.-% in polystyrene and 13.76 at.-% in poly(propylene) case. As discussed in the previous section, a careful study of the background gas was conducted to exclude contamination of the chamber and supply gas. XPS analysis of untreated samples after 5 min sputtering with argon ions was carried out as well. No traces of oxygen were found, ruling out the possibility that it migrated from the bulk of the sample

the first place of attack for the reactive species causing hydrogenation or oxidation. Other possibilities include cleavage of the rings from the main chain or ring opening, and hence loss of the aromatic character of polystyrene within the XPS penetration depth. Furthermore, peak broadening and the characteristics shifts for carbon connected to singly and doubly bonded oxygen suggest that the chemical surface structure of the polymer is

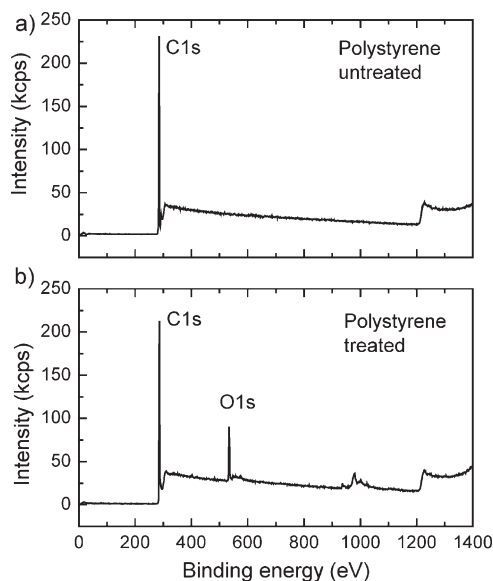


Figure 9. Survey spectra of a) untreated and b) treated polystyrene. Plasma treatment conditions include duty factor of 10%, period of 20 ms and plasma exposure time of 5 min.

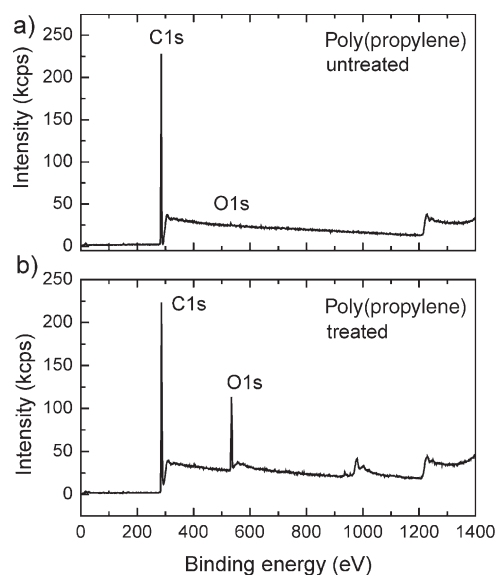


Figure 10. Survey spectra of a) untreated and b) treated poly(propylene). Plasma treatment conditions include duty factor of 10%, period of 20 ms and plasma exposure time of 5 min.

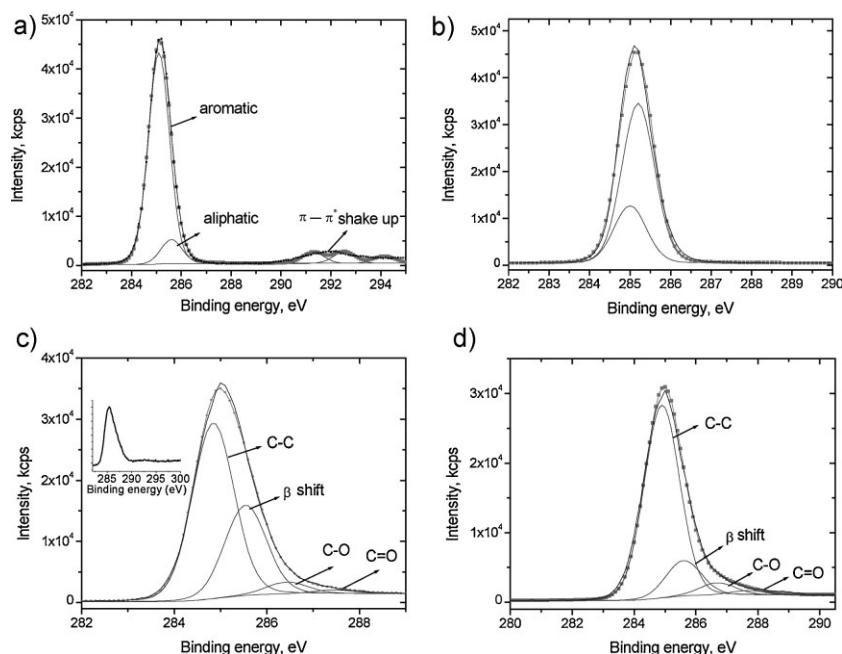


Figure 11. C1s spectra of untreated (a) polystyrene and (b) poly(propylene) and treated (c) polystyrene and (d) poly(propylene). Plasma treatment conditions include duty factor of 10%, period of 20 ms and plasma exposure time of 20 minutes.

changed. The existence of polar groups on the polymer surface will further restrict the bond rotation, which, combined with crosslinking, explains the increased glass transition temperature of the treated polystyrene. In the case of poly(propylene), peak broadening was observed, which, along with the reduction in glass transition temperature, suggests that chain scission is the dominant surface modification mechanism. It is well known that the nature of the chemical groups in the main chain determines the chain flexibility. For the case of poly(propylene), C–O and C=O were again observed, suggesting polar group formation on the surface. This could

explain why the glass transition temperature gradient before and after treatment was much more pronounced for polystyrene than for poly(propylene).

O/C ratios did not change with plasma period variation. O/C ratios as a function of treatment time and duty factor are presented in Figure 12 and 13. The actual values of the incorporated oxygen in all experiments are summarized in Table 2. The O/C ratio increases with time up to 10 min of treatment, to 0.15 for polystyrene and 0.18 for poly(propylene). However, further treatment caused the O/C ratio to fall. This might be due to surface rearrangement that reduces the possible places for oxygen attachment, and thus the level of oxygen incorporation. However, for 2 min of treatment, an increase in duty factor caused an almost linear increase in the O/C ratios for both polymers.

Another important question is how stable are the chemical modifications with time. To address this, a particular

polymer film sample was selected and its surface analyzed by XPS 10 min after treatment, 1.5 h after treatment, and a week after treatment. As shown in Figure 14, the oxygen incorporation remained almost constant during this span of time, suggesting that the chemical structure of the modified polymers is stable.

Discussion

The question of which plasma products – radicals, photons, or ions – most influence the polymer surface remains

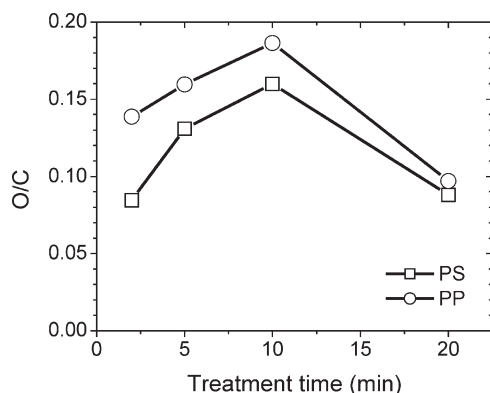


Figure 12. O/C ratio as a function of treatment time for polystyrene (PS) and poly(propylene) (PP). Plasma treatment conditions include duty factor of 10% and period of 20 ms.

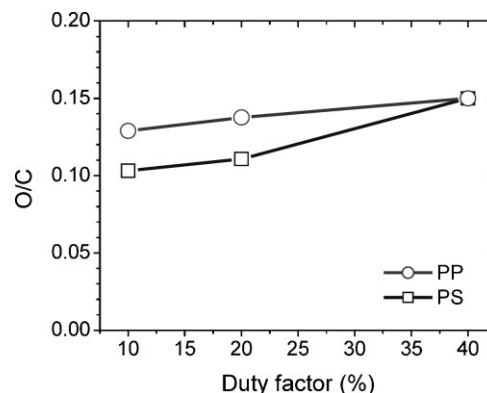


Figure 13. O/C ratio as a function of duty factor for polystyrene (PS) and poly(propylene) (PP). Plasma treatment conditions include exposure time of 2 min and period of 10 ms.

Table 2. Summary of carbon and oxygen atomic concentrations after plasma exposure.

Duty factor	Period	Pulse width	Treatment time	Polystyrene		Poly(propylene)	
				C1s at.-%	O1s at.-%	C1s at.-%	O1s at.-%
10	10	1	2	90.64	9.35	88.57	11.42
20	10	2	2	90.04	9.97	87.89	12.1
40	10	4	2	86.5	13.16	86.94	12.75
10	20	2	2	92.22	7.79	87.82	12.18
10	20	2	5	88.42	11.58	86.24	13.76
10	20	2	10	85.91	13.74	84.29	15.71
10	20	2	20	91.91	8.09	91.16	8.84

controversial. Numerous studies in argon discharges have been conducted. Barton et al.^[25,26] compared the role of VUV photons and ions on polymer surfaces in a RF plasma. They concluded that ions play the major role in polystyrene surface modification. The same conclusion was reached by Groning et al.^[27] On the other hand, Vallon et al.^[28] assumed that UV photons are primarily responsible. Tajima and Komvopoulos^[29] performed a series of experiments to determine the role of photons, metastables and ions. They concluded that radicals and photons are more important than ions.

Compared to plasma discharges, electron beam generated plasmas have distinctly different relative concentrations of these products. In order to understand the differences, consider how the products are formed and in particular how electron energy is spent. In discharges, the electron energy distribution falls off rapidly at high energy, so far more electrons can excite the gas than ionize it; the excitation rate thus greatly exceeds the ionization

rate. For example, if the energy distribution is Maxwellian, the ionization rate varies as $\exp(-W_i/T_e)$ whereas the metastable and photon production rates vary as $\exp(-W_m/T_e)$ and $\exp(-W_{ex}/T_e)$ where W_i , W_m , W_{ex} are the ionization, metastable, and optically allowed excited energies, respectively, and T_e is the electron temperature. In argon $W_i = 15.76$ eV, $W_m = 11.55$ eV, and $W_{ex} = 11.6$ eV (for W_m and W_{ex} , we have assumed the lowest metastable and optically allowed levels). The exponential factors thus differ by roughly one order of magnitude at $T_e = 2$ eV, so discharges typically produce more metastables and photons than ions. Swarm calculations^[30] support this claim. Therefore, during discharge plasma exposure, the flux of metastables and photons can easily exceed the flux of ions at the substrate, even at low pressure.

In electron beam plasmas, there are two classes of electrons: the primary beam electrons and the lower energy secondary electrons, which include the plasma electrons. For 2 keV electrons, the electron impact ionization cross section is an order of magnitude higher than the excitation cross sections and 3 orders of magnitude higher than the metastable cross sections. Vasenkov^[31] has computed the mean energy required to form a number of optically allowed states and a composite metastable state. Using this information, one can determine the relative production rates. For example, the number of metastables created per ion equals the ratio of the two mean energies. From this work, it can be found that roughly 11 ions are created for every metastable. For the optically allowed states, the relative production varies between roughly 8 and 65 ions per excited state. Similar conclusions were reached by Bretagne et al.^[32] using more states, and their calculations indicate that roughly one metastable is created for every 20 ions produced. Thus, in electron beam generated plasmas, the largest flux at the polymer substrates will be ions rather than metastables or photons.

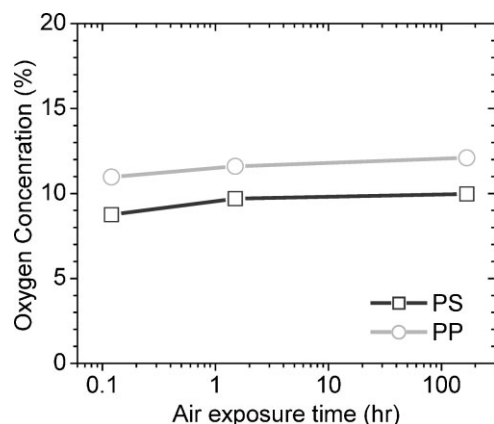


Figure 14. Stability of the chemical structure of the modified polystyrene and poly(propylene). Plasma treatment conditions include duty factor of 10%, period of 10 ms and plasma exposure time of 2 min.

The ion flux in the present experiments can be estimated using:

$$F_+ \cong D_a \cdot n_i / l \quad (2)$$

where D_a is the ambipolar diffusion coefficient, n_i is the ion density at the beam center, and l is the distance from the center to the processing stage. As previously shown,^[33] $D_a \approx 2 \times 10^3 \text{ cm}^2 \cdot \text{s}^{-1}$, $l = 2.5 \text{ cm}$, and $n_i = 10^{11} \text{ cm}^{-3}$ and thus $F_+ \approx 10^{14} \text{ cm}^2 \cdot \text{s}^{-1}$. The metastable and photon fluxes are roughly one order of magnitude lower than the ion flux for the reasons already explained above. For comparison, the ion flux measured by Barton et. al.^[25,26] using an RF source at 50 mTorr was roughly $10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$, which is an order of magnitude lower than the ion flux in electron beam plasmas. However, the ion energy fluxes are comparable, because the kinetic ion energy in their work was one order of magnitude larger ($\approx 30 \text{ eV}$ versus 3 eV). Barton et al. also determined that the photon and ion fluxes were of the same order of magnitude.

Based on the discussion above, the relative fluxes of species in discharges and electron beam generated plasmas are different. If indeed the radicals and/or photons are primarily responsible for controlling the polymer surface modification, then our experiments would have been less successful in producing chemical changes at the surface. However, this is not the case, in that the chemical alteration of the polymer surface layer is similar to the published results using a RF discharge. The only major difference between the electron beam produced plasmas used here and discharges is the change in surface morphology. Specifically, the surface roughness is significantly increased when using discharges, whereas it is unchanged or even reduced when exposed to electron beam plasmas. This difference is attributed to the lower incident ion energies in the latter case. We believe that beam-produced plasmas thus provide unique opportunities in material processing, especially for biosensors and flexible electronic devices, where surface roughness is a significant concern.

Conclusion

Pulsed, electron beam generated plasmas produced in argon were used to investigate the modifications of homopolymers. The equilibrium water contact angle for both polymers was halved after plasma treatment, indicating that the surface energy was significantly increased. These changes are believed to occur because of polar group incorporation after exposure of the plasma-treated polymers to air. The glass transition temperature measurements suggest that cross-linking was the major mechanism responsible for the chemical modification in

polystyrene, whereas methyl cleavage and chain scission is predominantly taking place in poly(propylene). The effect of the plasma parameters – plasma period, duty factor and plasma exposure time can be summarized as follows: Varying the plasma period allowed us to investigate if the long-lived species that exist in the afterglow have any effect on the polymer surface modification. We found that there was no pronounced effects in surface energy, etch rates, chemical or morphological modifications. These results suggest that the polymers were predominantly modified during the plasma pulse. Moreover, the variations of the duty factor (i.e. the plasma on time) produced a linear increase in the etch rates and oxygen incorporation and up to a 30% decrease in surface roughness in poly(propylene). The surface roughness decrease of polystyrene was not as large. The effect of plasma exposure time was more complex – initially it increased the etch rates and the oxygen incorporation (up to 10 min). After longer treatments, the etch rates and the O/C ratios were reduced. The surface roughness of poly(propylene) was decreased by 14%. Again, the decrease in the surface roughness of polystyrene was not as large. The results strongly suggest that the physiochemical changes at the polymer surface were ion-driven. In particular, it was shown that the ion flux is much larger than the flux of either metastables or photons in electron beam produced plasmas in contrast to conventional discharges. Equally important, the incident ion energy was only a few eV in these experiments. Thus, low-energy ions were found to be useful for modifying polymers, without the need of large fluxes of metastables and photons.

Acknowledgements: This work was supported by the *Office of Naval Research*. The authors are grateful to *Greg Pribil* from *J. A. Woollam Co.* who performed the glass transition temperature measurements. *EHL* appreciates the support of the *National Research Council*.

Received: August 28, 2008; Revised: January 14, 2009; Accepted: January 28, 2009; DOI: 10.1002/ppap.200800122

Keywords: AFM; ellipsometry; plasma treatment; polystyrene; poly(propylene); surface composition; surface energy; surface morphology; surface roughness; XPS; water contact angle

- [1] M. Shi, A. Selmani, L. Martinu, E. Sacher, M. Wertheimer, A. Yelon, *J. Adhes. Sci. Technol.* **1994**, *8*, 1129.
- [2] D. Hegemann, H. Brunner, C. Oher, *Nucl. Instrum. Methods Phys. Res. B* **2003**, *208*, 281.
- [3] J. Grace, L. Gerenser, *J. Dispersion Sci. Technol.* **2003**, *24*, 305.
- [4] M. Garrison, R. Luginbuel, R. Overney, B. Ratner, *Thin Solid Films* **1999**, *352*, 13.

- [5] L. Lopez, R. Gristina, G. Ceccone, F. Rossi, P. Favia, R. d'Agostino, *Surf. Coat. Technol.* **2005**, *200*, 1000.
- [6] R. M. France, R. D. Short, *Polym. Degrad. Stab.* **1994**, *45*, 339.
- [7] E. H. Lock, R. F. Fernsler, S. G. Walton, *Plasma Sources Sci. Technol.* **2008**, *17*, 025009.
- [8] S. G. Walton, D. Leonhardt, D. D. Blackwell, R. F. Fernsler, D. P. Murphy, R. A. Meger, *Phys. Rev. E* **2002**, *65*, 046412.
- [9] S. G. Walton, C. Muratore, D. Leonhardt, R. F. Fernsler, D. D. Blackwell, R. A. Meger, *Surf. Coat. Technol.* **2004**, *186*, 40.
- [10] R. France, R. Short, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3173.
- [11] E. H. Lock, S. G. Walton, R. F. Fernsler, Report NRL/MR/6750-08-9092. Copies may be ordered from the National Technical Information Service, Springfield, VA 22161. 2008.
- [12] X. Wang, X. Wang, Z. Chen, *Polymer* **2007**, *48*, 522.
- [13] E. Occhiello, M. Morra, P. Cinquina, F. Garbassi, *Polymer* **1992**, *33*, 3007.
- [14] O. J. Kwon, S. Tang, S. W. Myung, N. Lu, H. S. Choi, *Surf. Coat. Technol.* **2005**, *192*, 1.
- [15] S. Han, Y. Lee, H. Kim, J. Lee, J. Yoon, G. Kim, *Surf. Coat. Technol.* **1997**, *93*, 261.
- [16] M. C. Coen, G. Dietler, S. Kasas, P. Groening, *Appl. Surf. Sci.* **1996**, *103*, 27.
- [17] J. Hopkins, J. P. S. Badyal, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1385.
- [18] S. Tajima, K. Komvopoulos, *J. Phys. Chem. B* **2005**, *109*, 17623.
- [19] H. Gokan, S. Esho, Y. Ohnishi, *J. Electrochem. Soc.* **1983**, *130*, 143.
- [20] L. A. Pederson, *J. Electrochem. Soc.* **1982**, *129*, 205.
- [21] L. Singh, P. J. Ludovice, C. L. Henderson, *Thin Solid Films* **2004**, *449*, 231.
- [22] V. Zaporojtchenko, J. Zekonyte, F. Faupel, *Nucl. Instrum. Methods Phys. Res. B* **2007**, *265*, 139.
- [23] J. Zekonyte, J. Erichsen, V. Zaporojtchenko, F. Faupel, *Surf. Sci.* **2003**, *532–533*, 1040.
- [24] X. Jiang, C. Z. Yang, K. Tanaka, A. Takahara, T. Kajiyama, *Phys. Lett. A* **2001**, *281*, 363.
- [25] D. Barton, J. W. Bradley, D. A. Steele, R. D. Short, *J. Phys. Chem. B* **1999**, *103*, 4423.
- [26] D. Barton, J. W. Bradley, K. J. Gibson, D. A. Steele, R. D. Short, *J. Phys. Chem. B* **2000**, *104*, 7150.
- [27] P. Groning, O. M. Kuttel, M. Colland-Coen, G. Dietter, L. Schlapbach, *Appl. Surf. Sci.* **1995**, *89*, 83.
- [28] S. Vallon, B. Drevillon, F. Poncin-Epaillard, J. E. Klemberg-Sapieha, L. Martinu, *J. Vac. Sci. Technol. A* **1996**, *14*, 3194.
- [29] S. Tajima, K. Komvopoulos, *Appl. Phys. Lett.* **2006**, *89*, 124102.
- [30] C. M. Ferreira, J. Loureiro, A. Ricard, *J. Appl. Phys.* **1995**, *57*, 82.
- [31] A. V. Vasenkov, *Phys. Rev. E* **1985**, *57*, 82.
- [32] J. Bretagne, G. Calledé, M. Legentil, V. Puech, *J. Phys. D* **1986**, *19*, 761.
- [33] S. G. Walton, D. Leonhardt, R. F. Fernsler, *IEEE Trans. Plasma Sci.* **2005**, *33*, 838.